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## EXCITED STATE GEOMETRY OF AND RADIATIONLESS PROCESSES IN THE LOWEST $B_{3u}(n\pi^*)$ SINGLET STATE OF s-TETRAZINE

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High resolution absorption and laser induced emission spectra of the lowest  $B_{3u}(n\pi^*)$  singlet state of s-tetrazine- $h_2$  and - $d_2$  in a benzene crystal at 1.8 K are presented and discussed. The absorption spectrum with origin at  $17231\text{ cm}^{-1}$  ( $h_2$ ) is dominated by a progression in  $\nu_{6a}$  and a Herzberg-Teller origin which has been assigned as  $\nu_1$ . The absence of  $\nu_1$  in the emission spectrum is explained as being due to a destructive vibronic interference effect. The Franck-Condon envelope of the unique  $\nu_{6a}$  progression in emission is used for a determination of the excited state structure and the limitations of this procedure are examined. Direct lifetime measurements using a dye laser and single photon counting techniques show the fluorescence lifetime of s-tetrazine- $h_2$  and - $d_2$  to be shorter than 1.5 ns. From a deconvolution of the emission pulse of dimethyl s-tetrazine its fluorescence lifetime in the gas phase is found to be  $6.0 \pm 0.3$  ns. Through a comparison of the fluorescence quantum yield of s-tetrazine- $h_2$  and dimethyl s-tetrazine we calculate for s-tetrazine- $h_2$  a fluorescence lifetime of  $1.5 \pm 0.2$  ns and a fluorescence quantum yield of  $1.8 \times 10^{-3}$ . The ratio of the emissive lifetimes of s-tetrazine- $d_2$  and - $h_2$  was measured from relative fluorescence yields and found to be  $1.18 \pm 0.05$ . Photodissociation quantum yield studies on s-tetrazine- $h_2$ , - $d_2$  and dimethyl for excitation into the origin of the  $^1B_{3u}(n\pi^*)$  state show this yield to be in the range of  $1.3 \pm 0.3$ , and this could explain the low fluorescence yields of the s-tetrazines. The fluorescence quantum yields in the gas phase are found to vary among the vibronic levels of the  $^1B_{3u}$  state. This finding is in agreement with earlier measurements by Vemulapalli and Cassen, but the report by these authors that such quantum yield variations also occurred in the rovibronic structure is not confirmed.

### 1. Introduction

Among the well-known monocyclic azines, s-tetrazine, not unexpectedly, is the least stable and thus of great interest to a chemist. Indeed one of the more pertinent spectroscopic problems of the coming decade will be to relate spectral features such as line-widths and vibronic intensities to radiationless properties as photoinduced rearrangement and dissociation. In a recent review on radiationless transitions [1] the relationship among these features was demonstrated and the general theoretical framework outlined. The points just made had already been recognized by Chowdhury and Goodman [2] who were the first to observe fluorescence from this azine and characterized the emitting state as the lowest  $B_{3u}(n\pi^*)$  singlet state of s-tetrazine. These workers already noted that the fluorescence quantum yield was far below one and explained this as being due to inefficient intersystem

crossing to the lowest triplet state.

Earlier gas phase spectroscopic measurements by Mason [3] and Spencer et al. [4] on s-tetrazine had already noted the dominant appearance of the totally symmetric ring-bending  $\nu_{6a}$  mode in the absorption spectrum and established the origin of the system in the gas phase at  $5515\text{ Å}$ . From a rotational analysis of the  $J$ -structure of this origin on several s-tetrazine isotopes Merer and Innes [5] succeeded in establishing the geometry of s-tetrazine in this state.

Later work of Innes and co-workers [6] however showed large inertial defects to occur in the upper state which caused the structural determination of s-tetrazine in the  $B_{3u}(n\pi^*)$  singlet state to be unreliable. Recently Livak and Innes [7] reported observation of presumably the lowest triplet state of s-tetrazine in the gas phase, with the origin at  $13608\text{ cm}^{-1}$  and extracted from a Franck-Condon analysis the geometry of this excited state. This triplet state, on the basis of

vibronic features, was also assigned as being of  $B_{3u}$  spatial symmetry.

The study of the radiationless properties of s-tetrazine was taken up again by Vemulapalli and Cassen [8] who claimed to have observed a marked vibrational and rotational dependence on the radiationless decay of s-tetrazine. They interpreted the low quantum yield of fluorescence as being due to efficient intersystem crossing.

In a recent paper by McDonald and Brus [9] single vibronic level excitation by means of a dye laser into the singlet and triplet systems was reported and the fluorescence and phosphorescence decay was measured. An upper limit for the fluorescence decay time of 100 ns was given and the radiationless deactivation of the  $B_{3u}(n\pi^*)$  singlet state was interpreted as being due to a purely intramolecular internal conversion into the ground state. The 72  $\mu$ s lifetime of the triplet state was suggested to be possibly controlled by a radiative decay to a lower g-triplet state.

It must be concluded that the present status of our understanding of the spectroscopic properties (both radiative and radiationless) of s-tetrazine is far from satisfactory. Also insight into the connection between these properties and the known photochemical instability is missing. We have therefore planned a detailed study of the spectroscopic properties of s-tetrazine in the solid and in the gas phase. We have further encouraged some of our colleagues in the theoretical chemistry department to perform detailed ab initio calculations on s-tetrazine, to check on some of the speculations made and to guide our thoughts on this subject [10]. In this paper we wish to present some of our results obtained from a study of s-tetrazine- $h_2$ , - $hd$  and - $d_2$  in benzene mixed crystals at 1.8 K and in a low pressure gas at room temperature. An analysis of the singlet absorption and emission spectra is presented and the presence of  $\nu_1$  in the absorption spectrum interpreted as being caused by a constructive vibronic interference effect.

The emission spectrum, solely consisting of a progression in the ring bending  $\nu_{6a}$  mode, is used for a calculation of the upper state geometry. The limitations of this procedure, in view of the more complicated absorption spectrum, are discussed and suggestions are made as how more accurate structural data might be obtained.

The radiationless properties of the  $B_{3u}(n\pi^*)$  singlet

state were probed by measuring lifetimes, relative fluorescence and dissociation quantum yields of s-tetrazine- $h_2$  and - $d_2$  in both the benzene mixed crystal and the gas phase. The data from these measurements are compared with the corresponding ones of dimethyl s-tetrazine. Finally we present data which support previous suggestions [8] that the fluorescence quantum yield varies drastically among the vibronic structure in the gas phase spectrum. Our measurements however show no variation in fluorescence quantum yield for excitation in the rovibronic structure of the origin of the  $^1B_{3u}(n\pi^*)$  state.

## 2. Experimental

s-tetrazine and its deuterated isotopes were synthesized according to directions given by Spencer et al. [11] and the red crystals obtained after sublimation were stored in a freezer. Dimethyl s-tetrazine was prepared following the method of Skorjanetz and Kovács [12]. The mixed s-tetrazine in benzene crystals were grown in a cold room at a rate of 5 mm/h. The crystals were cut with a razor blade, but no attempts were made to orient them in these experiments, although polarization effects have been observed. The low temperature absorption spectra of s-tetrazine in benzene were taken with the exciting light passing first through the monochromator to avoid photo decomposition of s-tetrazine. A 1 meter 1704 Spex equipped with a grating blazed at 1  $\mu$  was used in the second order as the dispersing element for the absorption and emission spectra. The tunable dye laser used in these experiments consisted of a Molelectron DL-200 dye module and an AVCO C 950 pulsed nitrogen laser. The output pulse of this system had a width of 6 ns and spectral bandwidth of 0.2 Å. Either rhodamine 6G or fluorescein disodium salt was used as the lasing medium. A Brookdeal boxcar integrator was used as a gated amplifier to record the laser induced fluorescence. Pressures quoted in this paper were determined by expansion of a known volume of saturated s-tetrazine vapor into the measuring cell. The fluorescence cell and single photon counting equipment to study the laser induced decay have been described previously [13].

Relative fluorescence yield measurements in the gas phase were made by using a Bausch and Lomb

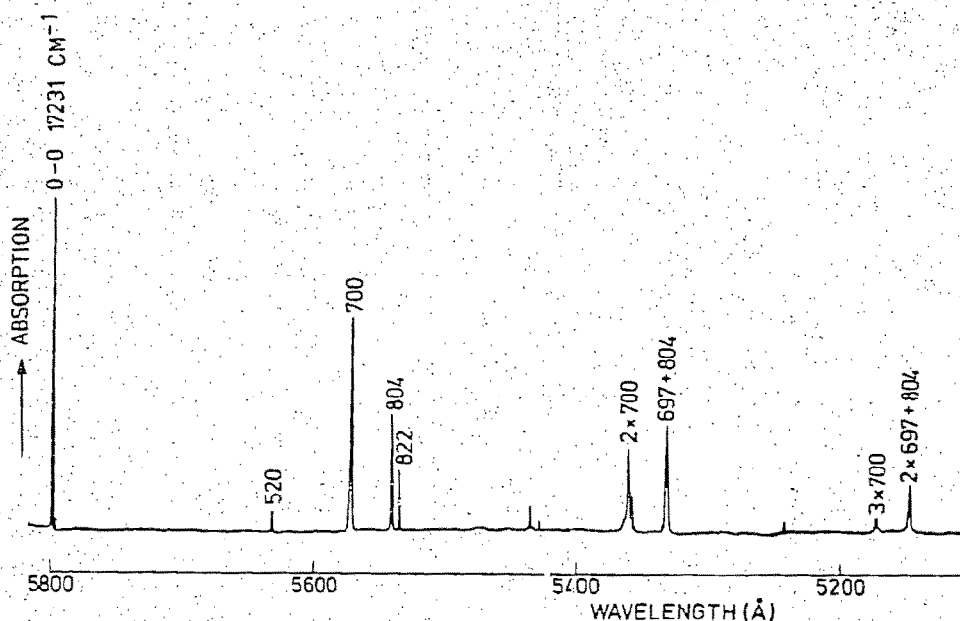


Fig. 1. Unpolarized absorption spectrum of s-tetrazine- $h_2$  in benzene at 1.8 K.

monochromator and an EMI 9558 B tube as photomultiplier. The relative yields quoted in this paper have been calculated by integration of the total fluorescence observed. Corrections have been applied for the through-put of the monochromator, spectral sensitivity of the photomultiplier and laser stray light (only few percent or less of total emission in all cases). All experiments were done at such a gas pressure that the optical density of the samples at the wavelength of interest was about 0.15.

### 3. Results and discussion

#### 3.1. The ${}^1B_{3u}(n\pi^*) \leftarrow {}^1A_{1g}$ absorption spectrum of s-tetrazine in benzene at 1.8 K

Fig. 1 shows the absorption spectrum of a mixed s-tetrazine- $h_2$  in benzene crystal at 1.8 K. The spectrum has been corrected for a broad underlying background caused by the xenon emission characteristic in this wavelength region. The first line in the absorption spectrum is found at  $17231\text{ cm}^{-1}$  and is coincident with the highest energy line in the fluorescence emission spectrum (section 3.2). The absorption at  $17231$

$\text{cm}^{-1}$  therefore definitely represents the true origin of an  $n\pi^*$  excitation which on several occasions [2,5] has been shown to be of  $B_{3u}$  spatial symmetry ( $N = x(b_{3u})$ ,  $M = y(b_{2u})$ ). In a benzene mixed crystal we thus observe an  $897\text{ cm}^{-1}$  red-shift of the origin with respect to the gas phase [5]. Higher resolution tracings of the origin in this crystal show this line to be as sharp as  $0.7\text{ cm}^{-1}$  with isotopic structure at  $3.3\text{ cm}^{-1}$  ( ${}^{15}\text{N}$ ) and  $3.7\text{ cm}^{-1}$  ( ${}^{13}\text{C}$ ) to higher energy, respectively. The deuteration shifts of  $7.5\text{ cm}^{-1}$  and  $15.0\text{ cm}^{-1}$  found for  $hd$ - and  $d_2$ -s-tetrazine, respectively, in this crystal are in excellent agreement with reported gas phase values [5].

The lay-out of the absorption spectrum is quite simple as can be seen in fig. 1. The spectrum is dominated by the progression forming mode  $\nu_{6a}$ . This mode equals  $701\text{ cm}^{-1}$  when based on the origin and reduces to  $697\text{ cm}^{-1}$  in combination with the  $804\text{ cm}^{-1}$  'false origin'. The absorption spectrum of s-tetrazine- $d_2$  in benzene looks quite similar, although an absorption corresponding to the  $822\text{ cm}^{-1}$  mode found in the s-tetrazine- $h_2$  spectrum is absent. Table 1 lists the prominent bands observed for both isotopes and also contains the assignments made by us.

The assignments were made on basis of known gas

Table 1

Line positions and vibrational assignment of the prominent bands in the  ${}^1B_{3u}(n\pi^*) \leftarrow {}^1A_{1g}$  absorption spectrum of s-tetrazine- $h_2$  and - $d_2$  in benzene at 1.8 K

$\lambda(\text{\AA})$	$\nu(\text{cm}^{-1})^a$	$\Delta\nu^a$	Analysis
5801.8	17231 (246)	0	origin
5632.0	17751	520 (523)	$2 \times \nu_{16a}$
5575.2	17932	701 (689)	$\nu_{6a}$
5574.9	17933	703 ( - )	
5543.2	18035	804 (815)	$\nu_1$
5537.7	18053	822 ( - )	$2 \times \nu_{16b}$
5483.1	18233	1002	
5442.2	18370	1139	
5435.7	18392	1161	
5416.4	18457	1226	
5366.0	18631	1400 (1378)	$2 \times \nu_{6a}$
5363.5	18639	1408 (1376?)	$2 \times \nu_{17b}?$
5336.8	18733	1502 (1496)	$\nu_1 + \nu_{6a}$
5245.1	19060	1829	
5172.9	19326	2095	
5170.7	19334	2103 (2065)	$3 \times \nu_{6a}$
5145.7	19428	2197 (2178)	$\nu_1 + 2 \times \nu_{6a}$

a) The numbers in parentheses refer to s-tetrazine- $d_2$  frequencies.

phase upper state vibrational frequencies [7,14] and most of them are close to the reported gas phase values. Of great interest is the triad of lines in the s-tetrazine- $h_2$  absorption spectrum found at 701, 804 and  $822 \text{ cm}^{-1}$  from the origin. We have assigned these lines as  $\nu'_{6a}$ ,  $\nu'_1$  and  $2 \times \nu'_{16b}$ , respectively, with corresponding gas phase values of 702.9, 784.4 and  $810.5 \text{ cm}^{-1}$  [7,14]. We suggest these lines to undergo extensive Fermi resonance coupling and in fact this may explain the unexpected intensity of  $2 \times \nu'_{16b}$  with respect to its gas phase intensity [15]. As was earlier noted, in s-tetrazine- $d_2$  no absorption feature corresponding to the  $2 \times \nu'_{16b}$  mode could be observed. In the gas phase it is found at  $691.1 \text{ cm}^{-1}$  [15] from the origin. We suggest its 'absence' in the benzene crystal to be partly due to its unfavourable zero order energy with respect to  $\nu_{6a}$  ( $689 \text{ cm}^{-1}$ ) and  $\nu_1$  ( $815 \text{ cm}^{-1}$ ). We observe here another feature characteristic of all absorption spectra of ortho-diazines, namely the increase of a vibrational frequency on deuteration. This feature led Hochstrasser and Marzzacco to their proposal of two nearby  ${}^1A_2(n\pi^*)$  states in the phthalazine absorption spectrum [16].

Innes and co-workers [17] however showed that a

similar anomalous deuteration shift was found in the pyridazine  ${}^1B_1(n\pi^*)$  absorption spectrum and this was interpreted by them as being due to anharmonic coupling among some totally symmetric modes. Later Stark effect measurements on the phthalazine absorption spectrum [18] indeed showed an alternative interpretation of the spectrum to be possible if the anomalous deuteration effect on the dominant vibrational mode could be explained otherwise. The increase of  $\nu_1$  from 804 to  $815 \text{ cm}^{-1}$  upon deuteration in the s-tetrazine absorption spectrum therefore is in line with observations in other diazine spectra and only its increase with respect to the gas phase values ( $784.4 (h_2)$ ;  $787.4 (d_2)$ ) [14] is somewhat unexpected. If  $\nu_1$  in the s-tetrazine absorption spectrum is vibronically active in mixing  ${}^1B_{3u}(n\pi^*)$  states with other states of the same symmetry, as was suggested in the case of pyridazine [17], the increase of  $\nu_1$  in the benzene mixed crystal with respect to its gas phase value may then be due to an increase in the gap between the interacting states.

There are some other weaker absorptions listed in table 1, which we have left unassigned. We feel that further work on oriented benzene mixed crystals is needed, before trustworthy assignments of these lines can be made.

Finally we would like to report that we have made accurate relative measurements of integrated absorption intensities of all modes assigned in table 1 on mixed crystals that contained both  $h_2$ - and  $d_2$ -s-tetrazine.

One important conclusion of these measurements was that the integrated intensity of  $\nu_1$  versus the origin was independent of deuteration. This is consistent with the slight dependence upon deuteration of  $\nu_1$  in the ground state but makes the suggested interpretation of the increase of  $\nu_1$  on deuteration doubtful [17]. We feel that a closer look at the anomalous deuteration shifts of these modes in ortho diazines is warranted.

### 3.2. The ${}^1A_{1g} \leftarrow {}^1B_{3u}(n\pi^*)$ emission spectrum of s-tetrazine in benzene at 1.8 K

Fig. 2 shows the fluorescence spectrum of s-tetrazine- $h_2$  in benzene at 1.8 K. The fluorescence was recorded by exciting the benzene mixed crystal with a dye laser resonant with the  $17932 \text{ cm}^{-1}$  s-tetrazine

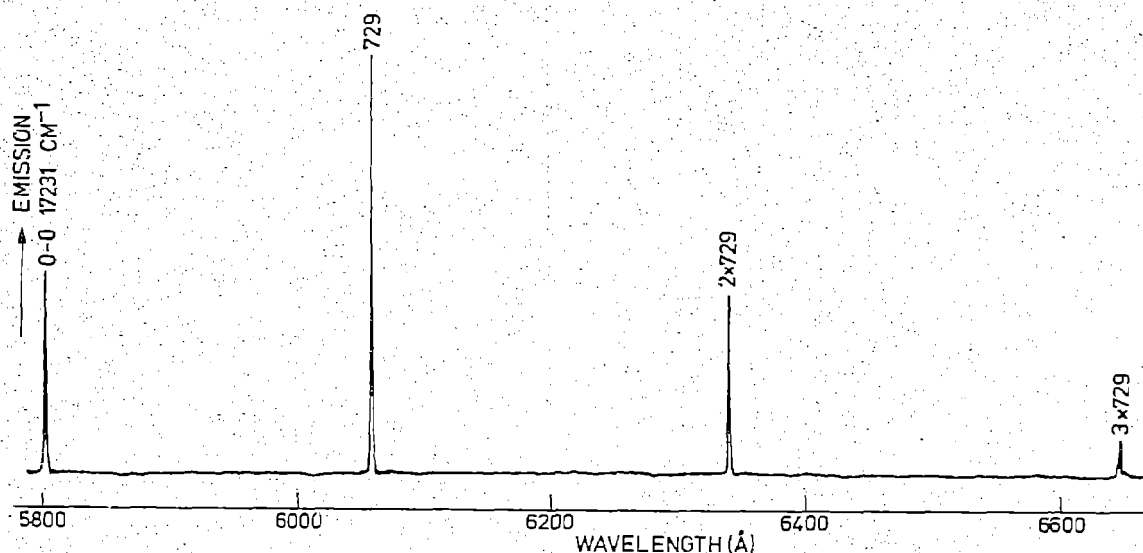


Fig. 2. Laser induced emission spectrum of s-tetrazine- $h_2$  in benzene at 1.8 K.

absorption ( $\nu'_{6a}$ ) and using a boxcar integrator as gated amplifier. The spectrum shown in fig. 2 is not what it seems. In reality several crystals were used to scan the emission spectrum with high amplification. Due to fast decomposition of the s-tetrazine under dye laser excitation (a matter of minutes!) the emission spectrum under most favourable conditions could only be searched through by using several crystals. Once it was established that the spectrum only showed the emissions of fig. 2 a final run was made, where the crystal was only excited when the spectrometer reached the emission positions. Fig. 2 thus represents the emission spectrum of non-decomposing s-tetrazine- $h_2$ , but uncorrected for the photomultiplier spectral response and grating efficiency.

As is shown in fig. 2 the fluorescence emission spectrum of s-tetrazine is extremely simple. Next to an origin at  $17231\text{ cm}^{-1}$  only a progression in  $\nu_{6a}$ , with vibrational frequency of  $729.3\text{ cm}^{-1}$ , is observed. This spectrum in fact is quite similar to the one found in the gas phase by Vemulapalli and Cassen [8] but these authors have not commented further upon it. We observe no lines in the emission spectrum other than those of the  $\nu_{6a}$  progression, although lines as intense as 5 % of the most intense one would not have escaped detection. Especially the absence of  $\nu_1$  ( $1017\text{ cm}^{-1}$  in the ground state [19]) in the emission spec-

trum is noticeable.

We have gone through the same procedures when scanning the fluorescence spectrum of s-tetrazine- $d_2$ . Again *only* a progression in  $\nu_{6a}$  based on the origin at  $17246\text{ cm}^{-1}$  was observed, with  $\nu_{6a}$  being reduced to  $715.6\text{ cm}^{-1}$ . Finally for s-tetrazine- $hd$   $\nu_{6a}$  was measured to be  $722.4\text{ cm}^{-1}$ . For both s-tetrazine- $h_2$  and - $d_2$  an accurate study was made of the relative intensities of the members of the  $\nu_{6a}$  progression. The relative intensities shown in fig. 3 represent  $I/\nu^4$ , where  $I$ , being the emission intensity, was corrected both for the spectral response of the photomultiplier and the known grating efficiency, and  $\nu$  is the emission frequency. Fig. 3 also contains the calculated relative intensities for an emitting one-dimensional displaced and distorted oscillator [20]. In these calculations we ignored the measured intensity of the origin, as its intensity is not very trustworthy due to appreciable re-absorption. For both s-tetrazine- $h_2$  and - $d_2$  we calculate from the emission spectrum an upper state displacement along  $\nu_{6a}$  of  $0.33 \pm 0.01 (\text{amu})^{1/2} \text{ \AA}$ .

### 3. The geometry of s-tetrazine in the $^1B_{3u}(n\pi^*)$ state

Merer and Innes [5] were the first to claim to have determined the ground and  $^1B_{3u}(n\pi^*)$  excited state

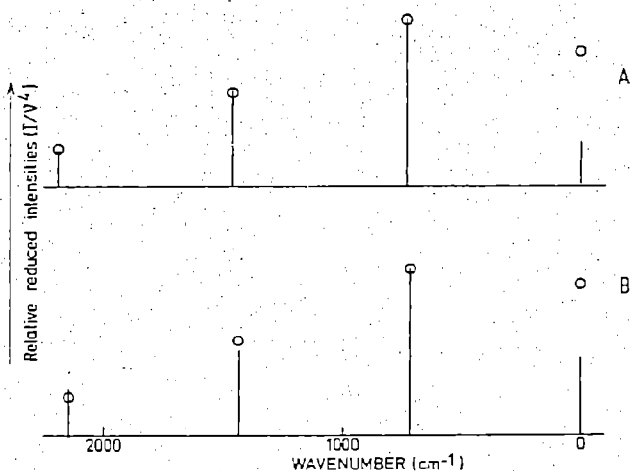


Fig. 3. Measured relative induced intensities ( $I/\nu^4$ ) of the  $\nu_{6a}$  progression in emission (sticks) and calculated ones (circles). Fig. 3a refers to s-tetrazine- $h_2$  with  $\delta(\nu_{6a}) = 0.333 \text{ (amu)}^{1/2}$ . A and fig. 3b represents the corresponding data for s-tetrazine- $d_2$  with  $\delta(\nu_{6a}) = 0.329 \text{ (amu)}^{1/2}$ . A.

geometries of s-tetrazine. This was done on the basis of a careful analysis of the rotational structure of the molecule in the gas phase. Their main conclusions were that on excitation the N—N bond is shortened by 0.11 Å, the C—N bond is lengthened by 0.05 Å and the NCN angle increased by 8°. In a later paper however Innes and co-workers [6] showed large inertial defects to occur in the excited states of the monocyclic azines. This observation makes their structural data obtained for s-tetrazine rather questionable. Using our experimentally found value for the displacement along  $\nu_{6a}$  of  $0.33 \text{ (amu)}^{1/2} \text{ Å}$  we calculate using the method of Livak and Innes [7] for the just quoted parameters respectively: 0.043 Å, 0.007 Å and 2.4°. These numbers are completely different from those reported by Merer and Innes [5], but are very close to those found by Livak and Innes [7] for the lowest  $B_{3u}(n\pi^*)$  triplet state (0.06 Å; 0.01 Å; 3.4°).

Our structural parameters are based on the Franck-Condon contour of the emission spectrum and on the one-dimensional oscillator model. While this seems in agreement with the emission data, the absorption spectrum clearly shows that this assumption is really an oversimplification of the situation.

Indeed  $\nu_{6a}$  is still dominant in absorption but an appreciable fraction of the absorption intensity is

stored in  $\nu_1$  and combinations of  $\nu_1$  with  $\nu_{6a}$ . The absence of  $\nu_1$  in the emission spectrum is tentatively explained by us as being due to destructive vibronic interference, an effect that has been recently described by Craig and Small [21] for the case of phenanthrene. For this effect to occur  $\nu_1$  should be a Herzberg-Teller active mode that vibronically couples the lowest  $^1B_{3u}(n\pi^*)$  state with higher  $\sigma\pi^*$  or  $\pi\sigma^*$  states of the same symmetry. The induced transition moment can either constructively or destructively interfere with the allowed moment and under favourable conditions this could lead to complete cancellation of the total transition moment in emission. The assignment of  $\nu_1$  in the absorption spectrum as a 'false origin' is in agreement with the absence of its overtone and in line with an earlier suggestion for the occurrence of the corresponding mode in pyridazine [17]. We hope in the near future to present a more detailed analysis of this vibronic interference effect in the s-tetrazine spectrum as in principle it will provide us with the induced transition moment(s) and the displacements in the upper state along  $\nu_{6a}$  and  $\nu_1$ . From these displacements more reliable excited state structural data could be derived than the ones presented. At present this seems to be the only way to determine the excited state geometry of s-tetrazine more accurately.

#### 4. Radiationless processes in the $B_{3u}(n\pi^*)$ singlet state of s-tetrazine

We have made an accurate study of the fluorescence lifetimes, relative fluorescence quantum yield and photodissociation quantum yields of s-tetrazine- $h_2$  and - $d_2$  in both the gas and solid phase. Similar measurements were made for dimethyl s-tetrazine. A knowledge of these data seems indispensable for a better understanding of the non radiative properties of these molecules. A tunable dye laser with a pulse length of 6 ns was used for excitation and single photon counting equipment was used to record the fluorescence decay curves. Fig. 4 shows the laser pulse as registered with the single photon counting technique. The fluorescence decay curves of s-tetrazine- $h_2$  and - $d_2$  in the solid and gas phases were measured under the same conditions but found to be indistinguishable from the laser pulse itself. A computer simulated convolution of the laser pulse and an exponentially decaying signal

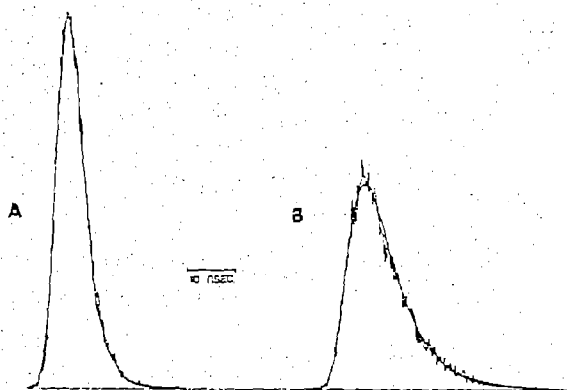


Fig. 4. Time profile of (a) the laser stray light and (b) fluorescence decay curve of dimethyl s-tetrazine in the gas phase excited at 5715 Å. The solid curve in fig. 4a represents the 'smoothed' laser pulse used to generate the convolution (solid curve) in fig. 4b. A 6 ns emission decay constant was used in this convolution.

showed the upper limit of the fluorescence decay time to be 1.5 ns. Fig. 4 also shows the laser induced fluorescence decay of dimethyl s-tetrazine in the gas phase when excited at 5715 Å. From a deconvolution of this curve we find for the fluorescence decay time of dimethyl s-tetrazine  $6.0 \pm 0.3$  ns, which is close to that (4.1 ns) reported by Chowdhury and Goodman [2] for this decay in a solution at room temperature.

We have also measured in the gas phase the relative quantum yields for emission of dimethyl s-tetrazine and s-tetrazine- $h_2$  and found this ratio to be  $4.0 \pm 0.3$  for excitation in the respective electronic origins. Assuming this difference in yields only to be due to a difference in non radiative processes in these molecules one calculates the fluorescence lifetime of s-tetrazine- $h_2$  to be  $1.5 \pm 0.2$  ns. From the integrated gas phase oscillator strength of  $5.4 \times 10^{-3}$  [9] a radiative lifetime of  $\approx 850$  ns is calculated. From these numbers we thus calculate an absolute fluorescence quantum yield for s-tetrazine- $h_2$  of  $1.8 \times 10^{-3}$ .

Further information about the radiationless process in the singlet state was obtained from relative fluorescence quantum yield studies on the per-proto and per-deutero isotopes of s-tetrazine. In the solid this was accomplished by comparing the origin absorption spectra of benzene mixed crystals containing equal amounts of s-tetrazine- $h_2$  and - $d_2$  with laser induced excitation spectra of these crystals. These measure-

ments showed the fluorescence quantum yield of s-tetrazine- $d_2$  to be larger than that of s-tetrazine- $h_2$ . This result was fully confirmed by similar gas phase experiments where photodissociation does not limit the accuracy. From these experiments we find the ratio between the fluorescence decays of  $d_2$ - and  $h_2$ -s-tetrazine to be  $1.18 \pm 0.05$  for excitation into the Q-branch of the origins of these isotopes.

So far, the low quantum yield for fluorescence of s-tetrazine has been explained as either being due to a fast intersystem crossing process to the triplet state [8] or to internal conversion [9] into the ground state. Another possibility, namely radiative decay to a lower g-type state was discussed by McDonald and Brus [9], but ab initio SCF molecular orbital calculations by Jonkman et al. [10] show this to be very unlikely. These calculations in fact show that either in the localized or delocalized description of the  $n\pi^*$  excitations, both the lowest triplet and singlet state include  $a_u \rightarrow b_{3g}$  orbital promotions. We have searched extensively for the s-tetrazine in benzene mixed crystal at 1.8 K for phosphorescence out of the lowest triplet state, while exciting with a dye laser into the origin of the singlet system, but have not been successful. This experiment shows that efficient intersystem crossing to the lowest triplet state cannot be the reason for the low fluorescence quantum yield of s-tetrazine.

Hochstrasser and Li [22] showed the very low fluorescence quantum yield of the lowest azulene singlet state to be due to an ultrafast decay into the ground state and indeed s-tetrazine might fluoresce inefficiently for the same reason.

We observed in the mixed s-tetrazine/benzene crystal the guest to decompose very rapidly under excitation, and this suggested a measurement of the photodissociation quantum yield of s-tetrazine. We have done such a measurement in the gas phase, where the loss of fluorescence and decay in absorption were measured under continuous excitation in the Q-branch of the origin.

The number of photons emitted by the dye laser was calculated from the energy output measured by an actinometer. In this way the photodissociation quantum yields of s-tetrazine- $h_2$ , - $d_2$  and -dimethyl were measured and all found to be in the range of  $1.3 \pm 0.3$ .

If dissociation takes place directly from the excited state the fluorescence lifetimes are determined by the competition between dissociation and internal



conversion. At present however we cannot exclude photodissociation to take place from the vibrationally excited ground state. In this case the fluorescence lifetimes indeed represent the rates at which interconversion into the ground state takes place [9].

Finally we wish to report that we have made relative fluorescence yield measurements of s-tetrazine in the gas phase under excitation in the absorption maxima of the P, Q and R-branch of the origin. The fluorescence yields in these maxima were measured for identical absorption depths. Vemulapalli and Cassen [8] report a 40 to 50 % higher yield under excitation in the P and R-branches versus excitation in the Q-branch. Our measurements show no significant variation in fluorescence yields among the different branches, in fact on the contrary we found the fluorescence yields in the P and R-branches to be about 10 % less than in the Q-branch. As our measurements assume Beers law to hold for an excitation bandwidth ( $0.8 \text{ cm}^{-1}$ ) that is larger than the rotational splittings ( $\approx 0.4 \text{ cm}^{-1}$  in the P and R-branches and  $\approx 0.1 \text{ cm}^{-1}$  in the Q-branch) we do not make any discussion about the significance of this finding.

We have also measured relative fluorescence yields for excitation in the hot bands which surround the electronic origin of s-tetrazine. Vemulapalli and Cassen [8] again report large variations among the fluorescence quantum yields for excitation into these hot bands. Our measurements indeed show these variations to occur; e.g., we have measured the relative fluorescence yields for excitation in  $\nu_{16a_1}^1$ ,  $\nu_{16b_1}^1$  and the origin of s-tetrazine- $d_2$ . We found the fluorescence yields for excitation in the origin and  $\nu_{16a_1}^1$  to be equal and the fluorescence yields for excitation in  $\nu_{16b_1}^1$  to be 90 % higher. Our absolute fluorescence yields though are calculated to be a factor of 10 smaller. We have planned a more detailed study of these fluorescence quantum yields and (presumably) lifetime variations among the vibronic structure of the  ${}^1B_{3u}(n\pi^*)$  state of s-tetrazine.

#### 4. Conclusions and prospects

One of our preliminary conclusions, obtained from the mixed crystal absorption and emission experiments, is that s-tetrazine is not so distorted in the  $B_{3u}(n\pi^*)$

singlet state as was previously inferred from a rotational analysis of the origin absorption. Definite conclusions however cannot be made until the Franck-Condon envelope of the absorption and emission spectra can be generated from a set of internally consistent vibrational displacements and induced transition moments. The excited state dynamics of s-tetrazine have been shown to be governed by a fast ( $\leq 1.5 \text{ ns}$ ) non radiative process. This process can be either dissociation, internal conversion into the ground state or a competition between these two. The ultimate fate of an s-tetrazine molecule however is dissociation, upon excitation into the  $B_{3u}(n\pi^*)$  singlet state. The presence of a (quasi)continuum of the dissociative state in the region of the  ${}^1B_{3u}(n\pi^*)$  absorption spectrum could cause Fano type [23] perturbations in the absorption spectrum of s-tetrazine and this seems to be an interesting point for further optical studies on this molecule. An interesting question is whether photodissociation also occurs from the lowest triplet state of s-tetrazine. The short lifetime ( $72 \mu\text{s}$ ) measured by McDonald and Brus [9] for s-tetrazine in the gas phase might be a manifestation of such a process. We plan to study this problem in both the gas and solid phase and hope to observe phosphorescence in the isotopic mixed crystal of s-tetrazine by directly exciting the lowest triplet state with a dye laser. Further fluorescence and dissociation quantum yield studies upon selective excitation in the vibronic structure of the  $B_{3u}(n\pi^*)$  singlet state are now underway. The results from this study might provide the answer to the question from which electronic state s-tetrazine dissociates and which vibration acts as the promoting mode in this process.

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## Note added in proof

Just recently we have been able to obtain the pure crystal s-tetrazine singlet-triplet absorption and dye laser induced phosphorescence spectrum of s-tetrazine in an isotopic mixed crystal. The origin of the triplet system in the pure proto crystal is located at  $14095\text{ cm}^{-1}$ , no factor group splitting is observed, and the spectrum is completely dominated by an intense  $\nu_{6a}$  progression ( $\nu'_{6a} = 718\text{ cm}^{-1}(h_2)$ ;  $703\text{ cm}^{-1}(d_2)$ ). The phosphorescence spectrum again only showed the  $\nu_{6a}$  progression ( $\nu''_{6a} = 733\text{ cm}^{-1}(h_2)$ ;  $718\text{ cm}^{-1}(d_2)$ ) and from the Franck-Condon envelope of this progression we calculate an upper state displacement along  $\nu_{6a}$  of  $0.29 \pm 0.02\text{ (amu)}^{1/2}\text{ \AA}$ . The phosphorescence decay times at 1.8 K in the isotopic mixed crystal were measured to be  $61\text{ }\mu\text{s}(h_2)$  and  $144\text{ }\mu\text{s}(d_2\text{-X-trap})$ .

The details of these experiments will be presented in a future paper.

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